

Absolute Spin Magnetic Moment of FeF₂ from High Energy Photon Diffraction

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The magnetic spin structure factor of FeF₂ has been directly determined from high energy magnetic x-ray diffraction at 115 keV photon energy. A pure spin moment of $\mu = 4.01(5)\mu_B$ was observed, which agrees very well with the spin moment of the free Fe²⁺ ion and differs significantly from values of the total magnetic moment obtained by other methods. The magnetic phase transition of FeF₂ has been carefully investigated and values for the critical exponent of the order parameter obtained by other techniques have been confirmed.

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The separation of the spin and orbital contribution to the magnetic moment in magnetic materials has for a long time been a challenge in experimental condensed-matter physics. The separate knowledge of both components provides important information about spin-orbit and Coulomb interactions and crystal field effects in the solid. In the last years new methods using x rays have been developed which offer great opportunities in this direction.

For antiferromagnets, a separate determination of spin and orbital moment can be performed in the medium energy range of x-ray diffraction using polarization analysis. The rather complicated polarization dependence of the magnetic scattering cross section allows the determination of the L/S ratio as a function of the momentum transfer. Results from this technique have been published for different materials [1–4]. For ferromagnetic materials other methods exist such as magnetic x-ray circular dichroism (MXCD) [5–7], which strongly rely on theoretical models available, or x-ray diffraction using circularly polarized x rays [8,9].

Here, we present results of a magnetic diffraction experiment on antiferromagnetic FeF₂ with 115 keV photons, where the magnetic scattering cross section depends only on the spin component perpendicular to the diffraction plane and which is independent from the polarization of the x rays. This allows one to measure the absolute spin magnetic moment without polarization analysis. Combined with antiferromagnetic resonance and neutron diffraction results found in the literature [10,11], this method can be used to determine the spin and orbital contribution to the magnetic moment separately and model free. In addition, at these energies correction factors for absorption and polarization are negligible due to the small scattering angles. The method of high energy magnetic x-ray diffraction has been developed on MnF₂ [12–15] during the last few years.

Recently, an attempt has been undertaken to perform a spin-orbit separation on chromium [16] for which the orbital moment is very small. Because of the fact that the magnetic domains are not equally distributed in chromium,

an absolute determination of the magnetic moment was not possible. Instead, the Q dependence of the magnetic form factor was used. This turned out not to be as precise as the other methods for the L/S separation since the Q dependence of the magnetic spin- and orbital form factor are very similar. A more precise way of determining the pure spin form factor is the determination of the absolute magnetic spin moment. Previous work on a system without a contribution to the orbital momentum [15] has shown that an absolute determination of the magnetic moment is possible with nonresonant magnetic x-ray diffraction. This method is used in the present work on FeF₂. The crystal field quenching of the orbital momentum in this material is partially lifted by the LS coupling and an orbital contribution to the magnetic moment of about 12% is expected [10,11].

The differential scattering cross section for magnetic diffraction for high photon energies above 80 keV takes the following simple form [13]:

$$\frac{d\sigma}{d\Omega} = r_0^2 \left(\frac{\lambda_C}{d} \right)^2 |S_\perp|^2, \quad (1)$$

where r_0 is the classical electron radius, λ_C the Compton wavelength, d the interplanar lattice spacing, and S_\perp the Fourier transform of the spin component perpendicular to the diffraction plane. Because of the small prefactors in Eq. (1) and the small ratio of the number of electrons contributing to the magnetic signal to the total number of electrons in the unit cell, the magnetic signal is 6 orders of magnitude smaller than the signal from charge scattering. For nonzero Q values, the next significant contributions arise from spin and orbital contributions in the scattering plane perpendicular to the scattering vector. These are insignificant in our scattering geometry due to the experimental configuration. In addition these contributions are suppressed by $\sin\theta$ with respect to S_\perp in the scattering cross section [14]. The validity of Eq. (1) for energies larger than 100 keV has been demonstrated experimentally [15] and later confirmed theoretically [17]. Hence,

no orbital contribution to the magnetic signal occurs by this method. For neutrons, the diffracted intensity is proportional to the linear combination $\tilde{L}(\vec{Q}) + 2\tilde{S}(\vec{Q})$ of both the Fourier transforms of the spin $[\tilde{S}(\vec{Q})]$ and orbital angular $[\tilde{L}(\vec{Q})]$ momentum. Thus, by combining the results of high energy x-ray and neutron diffraction experiments, orbital and spin contributions can be separated without further theoretical assumptions.

To perform a reliable separation of spin and orbital contributions, the absolute intensity, and therefore the absolute magnetic moment, have to be determined very accurately. The magnetic intensity was put on absolute scale by normalization to the intensity of the charge scattering. The corresponding structure factors are known very accurately from γ -ray diffraction experiments [18]. Although the intensity of the charge and magnetic reflections differs considerably, this method can give results with a precision of better than 2%.

The experiment was conducted at the wiggler beam line of BESSRC-CAT at the Advanced Photon Source at Argonne National Laboratory [19]. As a monochromator an annealed Silicon-(311) crystal used in Laue-geometry ($\theta = 1.9^\circ$, $\Delta\lambda/\lambda = 0.003$) was chosen to diffract the wiggler beam into the experimental hutch providing a photon energy of 115 keV.

The sample was a prism shaped single crystal with a volume of 12 mm^3 . The $1 \times 1 \text{ mm}^2$ x-ray beam penetrated a sample thickness of $3.8(2) \text{ mm}$. The sample was mounted in a closed-cycle He cryostat with the c axis oriented perpendicular to the diffraction plane. FeF_2 has a rutile-type crystal structure with space group $P4_2/mnm$ and lattice constants of $a = 4.6933 \text{ \AA}$ and $c = 3.3007 \text{ \AA}$ at 11 K [18]. Thus, due to the fact that the magnetic moments in FeF_2 are aligned along the c axis of the tetragonal unit cell, the total magnetic spin moment was obtained by aligning the (001) plane in the diffraction plane [see Eq. (1)]. The thermal coupling of the sample to the sample holder was improved by surrounding the sample with heat-conducting grease. The temperature sensor was mounted on the sample holder as close as possible to the sample. The total mosaic spread was observed to be about 80 arcsec and the reflections are from two domains, both with a width of about 45 arcsec. The maximum intensity of the magnetic (100) reflection was 6000 cps over a background of 500 cps, as shown in Fig. 1. In addition to the magnetic reflections at the $(2n + 1 \ 0 \ 0)$ positions in reciprocal space multiple diffraction (Renninger) effects may occur at these positions as well. Therefore, Ψ scans (rotation of the scattering plane around the scattering vector) were performed to find regions which are free of Renninger reflections. The scans used to determine the intensity of the magnetic reflections were performed at different Ψ positions to confirm the reproducibility of the magnetic intensities. The data have been normalized to the signal of a photodiode monitoring the incident beam.

At the magnetic phase transition, the critical behavior was measured to ensure that the signal at low tempera-

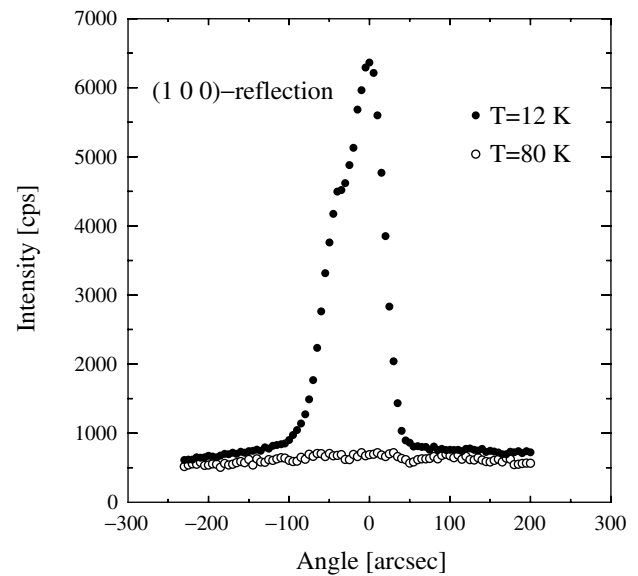


FIG. 1. Rocking curve of the magnetic (100) reflection. The solid circles show the reflection at 12 K; the open circles show a scan above the phase transition.

tures was purely magnetic. In addition, the critical region was investigated carefully. The measurements were performed on the magnetic (300) reflection. A power law for the reduced sublattice magnetization as a function of reduced temperature, $m = \tau^\beta$, was fit to the data in the temperature range between 70 and 75 K resulting in a critical exponent of $\beta = 0.329(18)$ (Fig. 2). This value agrees very well with the $\beta = 0.325(5)$ obtained from NMR measurements [20] and Mössbauer spectroscopy [21]. It

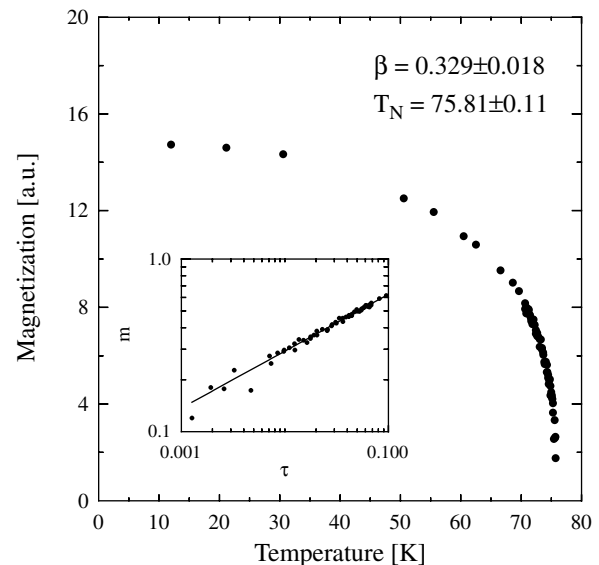


FIG. 2. The main graph shows the sublattice magnetization derived from the magnetic (300) reflection of FeF_2 as a function of temperature. The inset shows the reduced sublattice magnetization $m = m(T)/m(0)$ as a function of the reduced temperature $\tau = (1 - T/T_N)$ in double logarithmic scale. The line shows the fit of a power law to the magnetization as described in the text.

is in perfect agreement with the value calculated for the 3D Ising model: $\beta = 0.326$. The Néel temperature of $T_N = 75.8$ K is 2.3 K lower than determined in [20,21]. This difference, however, does not affect the determination of the critical exponent β , because only the reduced temperature τ is relevant.

Magnetic intensities were measured at the positions (100), (300), and (500). The magnetic structure factor was calculated according to the following equation:

$$|F_m|^2 = \frac{I_m}{I_c} \left(\frac{d}{\lambda c} \right)^2 \frac{\sin(2\theta_m)}{\sin(2\theta_c)} |F_c|^2 \frac{y_{\text{ext}}}{W_m}, \quad (2)$$

where I_m is the integrated magnetic intensity, I_c is the integrated intensity of the charge reflections, and θ_m and θ_c are the Bragg angles of the magnetic and the charge reflections, respectively. F_c is the charge density structure factor including the Debye-Waller factor, y_{ext} the corresponding extinction coefficient, and W_m the Debye-Waller factor of the magnetic reflection.

A correction for absorption within the sample is negligible since both the magnetic reflection and the charge reflections used for normalization are measured in virtually the same geometry. Because of the high photon energies, these reflections are less than 3° apart in the rotation of the sample which has very little effect on the absorption. The absorption length for 115 keV photons in the FeF_2 crystal is 11.2 mm. The structure factors of the charge reflections were obtained by γ -ray experiments at 11 K [18].

Since the magnetic signal is 6 orders of magnitude smaller than the charge signal, diffraction can be described within the kinematic regime. Therefore, no extinction correction is necessary for the magnetic reflections. For the charge reflections, which are used to normalize the data, a correction for extinction must be performed. Because of the limited dynamic range of the germanium solid-state detector, the charge intensity has been measured using calibrated iron filters. A dead time correction with $\tau = 3.5 \mu\text{s}$ was applied for the counting chain. The absorption coefficient $\mu_{\text{abs}} = 0.2203(2) \text{ mm}^{-1}$ of the iron filters for $E = 115$ keV has been determined experimentally. The intrinsic width of the rocking curve is $45(3)$ arcsec, which has been used to determine the extinction coefficient. The smallest extinction factor, obtained for the (400) reflection was $y_{\text{ext}} = 0.85(1)$ as calculated from Zachariasen's theory [22]. The extinction factors have been calculated under consideration of the statistical errors of the rocking curve width, the structure factor of the respective charge reflection, and the error in crystal thickness.

Equation (2) was used for the calculation of the magnetic structure factor for the magnetic (100) and (300) reflections. The mean value of the (200) and (400) charge reflection intensities was taken to normalize the magnetic intensities. The magnetic structure factors F_m are shown in Table I with their statistical errors. The (100) and (300) could be measured very reliably. At the (500) position the

TABLE I. The measured magnetic structure factor F_m as derived without correction for the zero-point motion is given. For the (100) and (300) reflections the corresponding corrected magnetic moment μ_{corr} is shown together with the mean magnetic moment $\bar{\mu}$.

Reflection	$\sin\theta/\lambda$ (\AA^{-1})	F_m (μ_B)	μ_{corr} (μ_B)	$\bar{\mu}$ (μ_B)
(100)	0.1065	3.522(57)	4.027(65)	
(300)	0.3196	1.605(28)	3.992(70)	4.01(5)
(500)	0.5327	0.548(98)		

Renninger reflections were dominant, resulting in a large systematic error for this reflection. Therefore, the (500) reflection has not been considered in the further discussion. The magnetic moment has been extrapolated using the magnetic form factors from [23] for the (100) and (300) reflections, only. To calculate the absolute magnetic moment, the zero-point motion of the magnetic moment has to be considered [24]. The correction to the spin moment has been calculated as $\langle S \rangle_0 = 0.98S$ by Ohlmann and Tinkham for FeF_2 [10]. The result obtained after this correction μ_{corr} is also given in Table I together with the mean value of the magnetic moment $\bar{\mu}$ from both the (100) and the (300) reflection. The absolute structure-factor dependence for all three magnetic reflections, corrected for zero-point motion, is shown in Fig. 3 as a function of $\sin\theta/\lambda$ together with $2S\langle j_0(Q) \rangle$, using the theoretical value for the spin $S = 2$. Here, $\langle j_l(Q) \rangle$ denotes a volume integral of the l th-order spherical Bessel function $j_l(Q)$ [23]. The magnetic structure factor for a neutron diffraction experiment

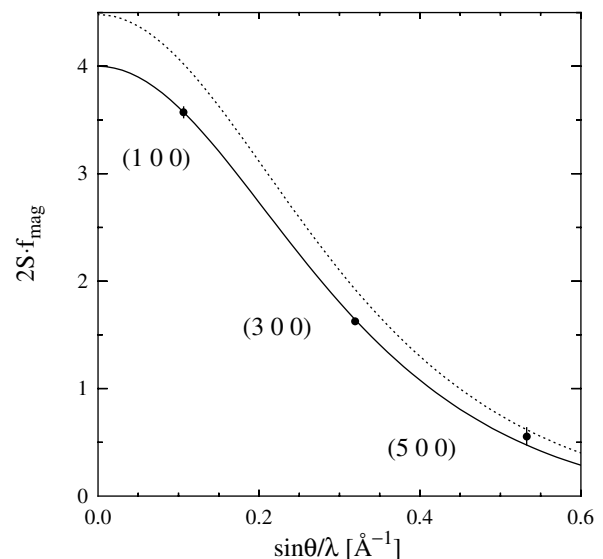


FIG. 3. The measured absolute magnetic structure factor $F_{hkl} = 2Sf_{\text{mag}}$ is shown as a function of $\sin\theta/\lambda$. The solid points show the experimental data of the (100), (300), and (500) reflections. The solid line shows the pure spin form factor $2S\langle j_0 \rangle$, whereas the dashed line shows the signal expected by neutron diffraction $2S[\langle j_0 \rangle + 0.12(\langle j_0 \rangle + \langle j_2 \rangle)]$ where an orbital contribution of 12% is assumed.

is [25]:

$$\begin{aligned} F_m^n(Q) &= g_z S f(Q) \\ &= 2S[\langle j_0(Q) \rangle \\ &\quad + (g_z/2 - 1)(\langle j_0(Q) \rangle + \langle j_2(Q) \rangle)] \quad (3) \end{aligned}$$

with the gyromagnetic ratio $g_z = \langle 0|L_z + 2S_z|0\rangle/S_z$, where $|0\rangle$ denotes the ground state wave function. The value obtained by Ohlmann and Tinkham by antiferromagnetic resonance is $g_z = 2.25(5)$ [10]. A more recent polarized neutron diffraction experiment gives $g_z = 2.23$ [11]. Both experimental results differ slightly from the first neutron diffraction result by Erickson who obtained $g_z = 2.31$ [26]. The value of the gyromagnetic ratio is equivalent to an orbital contribution of about 12% to the total magnetic moment. This corresponds to a total magnetic moment of $4.46\mu_B$ for the polarized neutron diffraction result. The corresponding magnetic structure factor $F_m^n(Q)$ as a function of $\sin\theta/\lambda$ from Eq. (3) is shown in Fig. 3, too. The values are considerably higher than the pure spin structure factor.

Our result for the pure magnetic spin moment of $\mu = 4.01(5)\mu_B$ supports the assumption that in FeF_2 the spin is $S = 2$ as in the free ion Fe^{2+} , which would be equivalent to a g factor of 2. Therefore, the additional 12% measured by other methods is of purely a orbital nature. There is no evidence for a reduction of the magnetic moment due to covalence effects as is discussed in [11].

For the first time, a spin-orbit separation was performed with high-energy x rays in combination with results obtained by other methods, e.g., neutron diffraction and antiferromagnetic resonance, on a system that shows a significant orbital momentum. In other studies done with these methods before, the system either has not shown an orbital contribution, or a separation was problematic because of the nonuniform distribution of the magnetic domains in the crystal. Since the form factor as a function of Q for the pure spin on the one hand and for spin and orbital contribution on the other are very similar in form, the obtained information about the absolute magnetic form factor is essential for a precise separation. Our result underlines the reliability of this method and shows clearly that such a separation is possible to a precision better than 2%. For future measurements it will be very important to look at other materials such as metallic transition metal

compounds or rare-earth metals, where the pure spin moment in the crystal differs from the moment of the free atom.

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